

# On the Coupling of Collisional Radiative Models and Boltzmann Equation for Atomic Transient Hydrogen Plasmas

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**Abstract.** Collisional-radiative model for atomic hydrogen has been coupled selfconsistently with the Boltzmann equation for electron kinetics to study the role of nonequilibrium electron distributions on the energy level kinetics. In particular, the role of second kind and electron-electron collisions in affecting both time dependent electron energy distributions and excited state population densities has been investigated.

## INTRODUCTION

The analysis of the emission spectra of a plasma is a powerful tool to investigate plasma composition and temperature. Quantitative analysis is based on the proportionality law that relate the amplitude of a line and the population density of the emitting level. New techniques, such as LIBS (Laser Induced Breakdown Spectroscopy), have renewed the interest in emission spectroscopy and collisional-radiative (c-r) models for atomic systems. In spatial homogeneous plasmas, the population of excited levels is determined by collisional processes (mainly electron-atom, e-A) and radiative decay. Collisional-radiative models calculate level distributions solving the system of master equations (one equation for any level) where the kinetic terms are due to e-A collisions, radiative decay and absorption.

The classical approach to c-r models is the QSS (quasi-stationary state) approximation introduced by Bates et al. [1]. This model is based on the assumption that the relaxation times of excited levels are order of magnitude shorter than ionization/recombination ones ( $\frac{\partial n_i}{\partial t} = 0 \forall i \neq 0, \frac{\partial n_1}{\partial t} = -\frac{\partial n_e}{\partial t} \neq 0$ ). In these conditions the level distributions are stationary with respect to electron and ion populations, simplifying the solution of the problem.

Soon after, however, it was recognized the importance of a time dependent integration of kinetic equations which are at the basis of the c-r models for situations characterized by very short macroscopic relaxation times. Time dependent solution of c-r models have been presented by Cacciatore et al. [2-5] for atomic H, O and N plasmas many years ago and more recently these plasmas [6-8] have been again studied for explaining new experimental situations (e.g. laser-plasmas interaction) in which a time dependent solution of c-r models seems to be necessary. In these papers [2-5], rate coefficients of e-A collisions are calculated approximating the eedf with the Maxwell distribution at a fixed temperature (free electron kinetics have been neglected). This assumption is realistic only if the ionization degree is high enough so that electron-electron Coulomb collisions (e-e) dominates the free electron kinetics.

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To applicate c-r models to the region in which the actual eedf differs appreciably from the Maxwellian form, in the present work we have coupled selfconsistently a collisional-radiative model for hydrogen atoms with the Boltzmann equation for free electron kinetics, calculating simultaneously level distributions and eedf. This model allows to investigate departures from equilibrium (Maxwell and Boltzmann) distributions during the thermal relaxation of the hydrogen plasma.

The aim of this paper is to analyze the conditions in which the electron energy distributions and the excited state populations differ from Boltzmann and Maxwell ones. Moreover, we are interested in studying the role of nonequilibrium electron distributions on the level kinetics. Finally, we intend to understand the influence of each elementary processes considered on both the time dependent electron energy distribution and the excited state population.

## METHOD OF CALCULATION

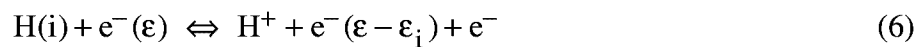
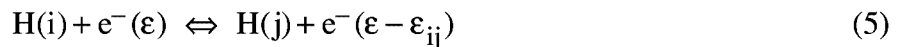
The system studied in this work is a plasma formed by atomic hydrogen (H), protons (H<sup>+</sup>) and electrons (e<sup>-</sup>). We assume the plasma is homogeneous and neutral (n<sub>e</sub>=n<sub>+</sub>). The levels are grouped by principal quantum number up to a maximum value of 25.

The plasma has been considered optically thin (photon absorption and photoionization have been neglected). The collisional-radiative model consists in a set of master equations, one for ion (n<sub>+</sub>) and electron (n<sub>e</sub>) molar fraction and one for each H level (n<sub>i</sub>)

$$\frac{dn_+}{dt} = \frac{dn_e}{dt} = -n_e \left( \sum_i R_i + n_e \sum_i Q_i \right) n_+ + n_e \sum_i S_i^e n_i \quad (1)$$

$$\frac{dn_i}{dt} = n_e \sum_{j \neq i} n_j K_{ji}^e - n_i n_e \left( S_i^e + \sum_{j \neq i} K_{ij}^e \right) + n_+ n_e^2 Q_i^e - n_i \sum_{j < i} A_{ij} + \sum_{j > i} A_{ij} n_j + n_+ n_e R_i \quad (2)$$

where A<sub>ij</sub> are the Einstein coefficients of the radiative decay (process 3), R<sub>i</sub> the rates of radiative recombination (process 4), K<sub>ij</sub><sup>e</sup> and K<sub>ji</sub><sup>e</sup>, with i < j, are respectively the rates of electron impact excitation (forward) and deexcitation (backward) (process 5), S<sub>i</sub><sup>e</sup> and Q<sub>i</sub><sup>e</sup> are the rates of electron impact ionization and three-body recombination (process 6)



$$\epsilon_{ij} = E_j - E_i \quad \epsilon_i = E_{ion} - E_i \quad (7)$$

where  $\epsilon_{ij}$  and  $\epsilon_i$  (eq. 7) represent the threshold energy of the transition  $i \rightarrow j$  and the ionization energy from the  $i$ -th level. Atom-atom and ion-atom collisions have been neglected assuming that the collision frequency of electron-atom is larger as both mean electron speed and electron impact cross sections are higher than heavy particle ones.

Rate coefficient for electron-atom collisions are calculated from eedf using the equation

$$K_e = \int_{E_t}^{\infty} f(\epsilon) \sigma(\epsilon) v(\epsilon) d\epsilon \quad (8)$$

where  $f(\epsilon)$  represents the eedf,  $\sigma(\epsilon)$  the cross section of the transition between atomic levels  $i$  and  $j$ ,  $v(\epsilon)$  the velocity of the electron of kinetic energy  $\epsilon$  and  $E_t$  the threshold energy of the process. The inelastic cross sections are taken from databases available on internet [9], as well as the Einstein coefficients.

Cross sections for superelastic collisions and three-body recombination are calculated using the detailed balance principle [10,11]:

$$\sigma_{deexct}(i, j, E) = \frac{g_j}{g_i} \frac{E}{E} \sigma_{exct}(j, i, E) \quad (9)$$

$$\sigma_{3b-recomb}(i, E) \frac{1}{n_e} = \frac{g_i}{2g_1^+} \left( \frac{h^2}{2\pi m_e k T_e} \right)^{3/2} \frac{E}{E} \sigma_{ioniz}(i, E) \quad (10)$$

where  $g_i$  is the statistical weight of the  $i$ -th level and  $g_1^+$  is the statistical weight of the ion ground state,  $h$  the Planck constant,  $m_e$  the electron mass,  $k$  the Boltzmann constant and  $T_e$  the electron temperature. Radiative recombination rate coefficients have been calculated according to the work of Johnson [12].

To introduce the non equilibrium free electron distributions we have solved the Boltzmann equation in the homogeneous and quasi-isotropic approximation developed by Rockwood [11,13] in the time dependent form

$$\frac{\partial f(\epsilon, t)}{\partial t} = -\frac{\partial J_E}{\partial \epsilon} - \frac{\partial J_{el}}{\partial \epsilon} - \frac{\partial J_{e-e}}{\partial \epsilon} - S_{in} - S_{sup} \quad (11)$$

where  $f(\epsilon, t)$  is the time dependent electron energy distribution function (eedf). The  $J$  terms on the right-hand side of eq. 11 are, respectively, the flux of electrons in the energy space due to the electric field ( $J_E$ ), elastic ( $J_{el}$ ) and electron-electron ( $J_{e-e}$ ) collisions and the  $S$  terms consider the jump of electrons in the energy space due to inelastic ( $S_{in}$ ) and superelastic ( $S_{sup}$ ) collisions. Ionization of atoms by electron impact (see eq. 6) has been considered in the electron kinetics as an inelastic process, neglecting the production of secondary electrons, while in the master equations (eqq. 1,2) this production has been taken into account. The numerical solution of this equation is widely described in literature (see for example [11, 13]).

The two systems of equations (one for electron kinetics and the other one for the collisional-radiative model) are strictly correlated; rate coefficients of electron impact processes are calculate from the eedf (see eq. 8) and the Boltzmann equation terms  $J$  and  $S$  (see eq. 11) depend on the level distribution. The simultaneous solution of electron, level and ionization kinetics (self-consistent model) is therefore

necessary. To calculate the time evolution of eedf and level distribution, we have used the first order implicit Euler method with step adaptive algorithm [14].

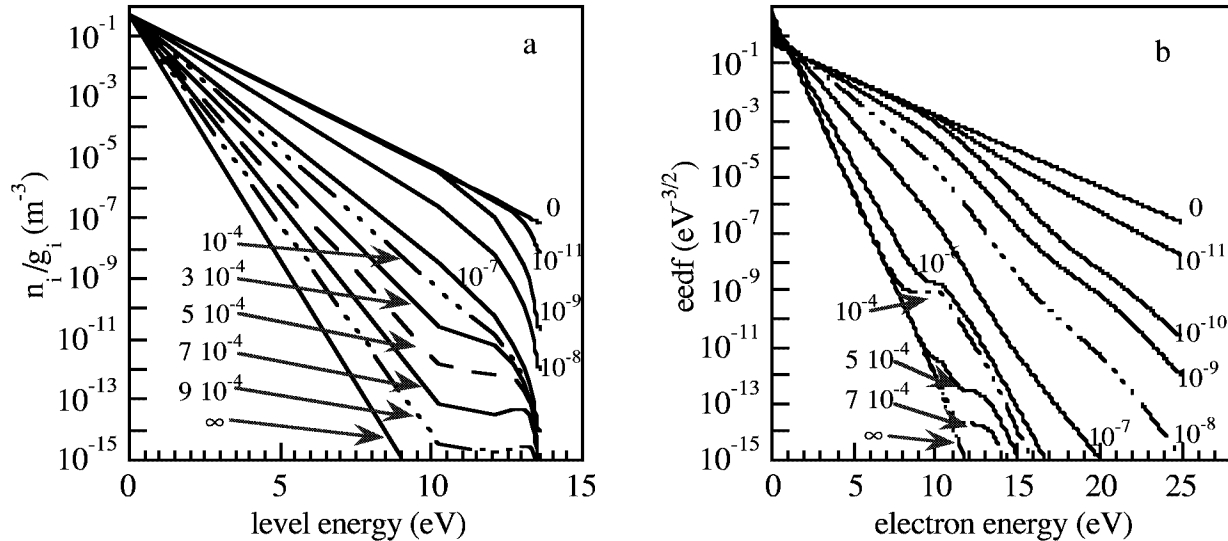
## RESULTS AND DISCUSSION

In this section we will investigate the relaxation of the level population and eedf in different conditions. The initial state is defined by fixing the gas temperature and pressure (maintained constant in all the integration interval), and assigning the initial value of ionization degree (ID), level population (a Boltzmann distribution with temperature  $T_i$ ) and eedf (a Maxwell distribution with temperature  $T_e$ ). In all the cases studied, the pressure and initial ionization degree have been fixed respectively to the value of  $P_0=1$  atm and  $ID_0=10^{-3}$ , and the cases considered differ for the value of  $T$ ,  $T_i$  and  $T_e$ . The gas temperature does not influence directly the level kinetics as atom-atom and atom-ion collisions have been neglected. On the contrary, the relaxation time of the eedf due to e-H and e- $H^+$  elastic collisions depends on gas temperature and, as a consequence, indirectly affects the level distribution through inelastic and superelastic collisions. We have analyzed three different conditions listed in table 1.

**TABLE 1.** Initial conditions for the cases studied

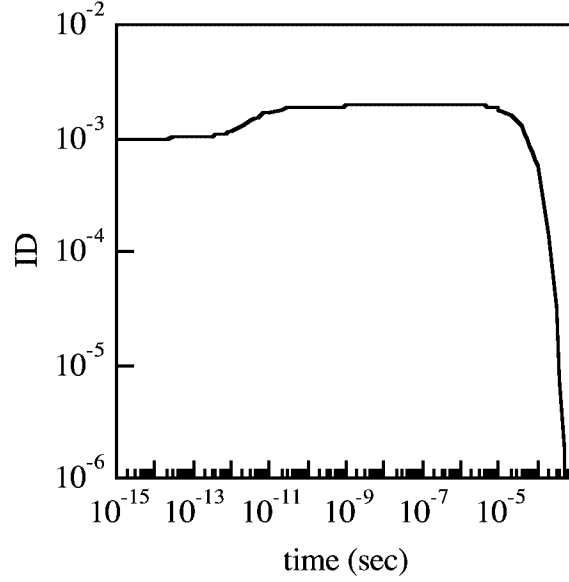
Label	T (K)	$T_i(t=0)$ (K)	$T_e(t=0)$ (K)	$ID_0$	$P_0$ (atm)
1	1000	10000	20000	$10^{-3}$	1
2	1000	10000	5000	$10^{-3}$	1
3	20000	10000	1000	$10^{-3}$	1

Figure 1 reports level population and eedf in the case 1 of table 1 ( $T < T_i < T_e$ ). The level population ( $n_i$ ) has been divided by the level statistical weight ( $g_i$ ) since for a Boltzmann distribution the logarithm of  $n_i/g_i$  shows a linear dependence on the level energy.



**FIGURE 1.** Time evolution of level distribution (a) and eedf (b) in the case 1 of table 1.

In this case we have  $T_e > T$  and therefore, due to electron-atom and electron-ion elastic collisions, eedf cools down to equilibrate the gas temperature. It can be observed that the electron distribution tail is non-maxwellian also at  $t < 10^{-9}$  s, while the electron temperature (which depends on the low energy eedf) does not change. Because  $T_e > T_i$ , inelastic collisions and electron impact ionization are the dominant processes in eedf and level population relaxation. Only when the electron distribution is cold enough ( $t > 10^{-6}$  s), the effects of superelastic collisions affect the eedf (see plateaux in fig 1 b).



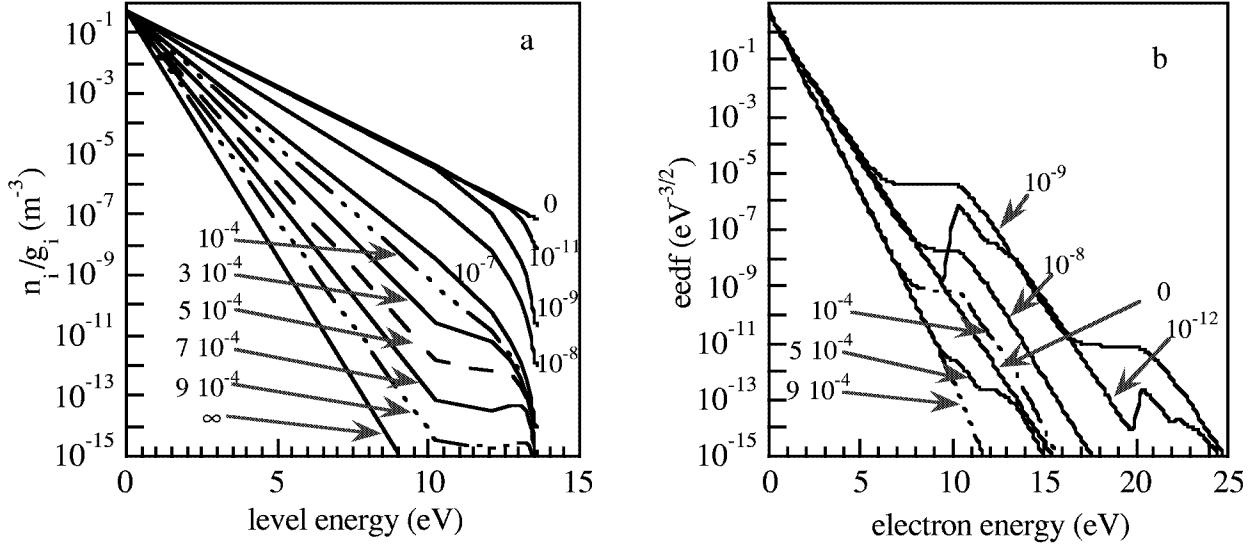
**FIGURE 2.** Time evolution of ionization degree in case 1 of table 1.

While the electron distribution is cooling, level distribution tail decreases, deviating from the Boltzmann distribution. For  $t < 10^{-9}$  s, level kinetics is dominated by ionization, while, for  $t > 10^{-4}$  s, the spontaneous emission for the low excited levels prevails and, at the same time, radiative recombination tends to repopulate the last excited levels. This behaviour can be confirmed by time evolution of the ionization degree (see fig 2). Ionization degree increases in the time interval  $10^{-12} \div 10^{-10}$  s, when ionization prevails, while it decreases for  $t > 10^{-5}$  s due to  $e-H^+$  recombination.

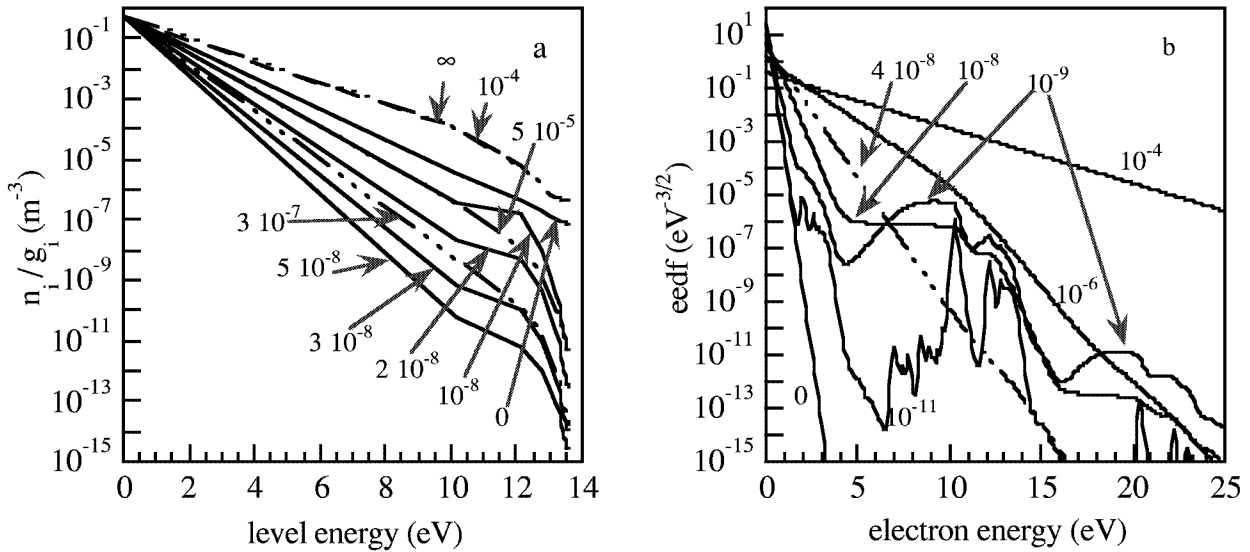
In case 2 of table 1 (fig. 3 a, b), electron temperature is higher than gas temperature but lower than internal temperature ( $T < T_e < T_i$ ). Initial ( $t=0$ ) and final ( $t=\infty$ ) eedfs are maxwellian on the contrary transient states show nonequilibrium distributions. Two different trends are observed: for  $t < 10^{-9}$  s, eedf warms up while it cools down for  $t > 10^{-9}$  s. Firstly ( $t < 10^{-12}$  s) two peaks appear (due to superelastic collisions) and, for longer time ( $t = 10^{-9}$  s), elastic collisions ( $e-H$ ,  $e-H^+$ ,  $e-e$ ) transform them in plateaux, resulting in the overpopulation of eedf tails. For  $t > 10^{-9}$  s, the energy exchange between electrons and excited levels equilibrates and therefore the eedf cools down slowly because elastic collisions push the eedf towards a maxwellian at the gas temperature. The level distribution cools down as well as does the eedf and also as a result of the radiative decay. Similarly to case 1, for sufficiently long times, the tail of level distribution is overpopulated with respect to the Boltzmann one when the radiative recombination becomes more important than ionization.

Very interesting results are obtained when the initial electron temperature of the plasma is lower than both internal and gas temperature ( $T_e < T_i < T$ ), as in case 3 of table 1 (fig 4 a, b). Again, initial and final eedf are maxwellian but intermediate distributions are very far from equilibrium. In particular, at short

time ( $t=10^{-11}$  s) the distribution tail shows sharp peaks because of superelastic collisions and at longer times ( $t=10^{-8}$  s) plateaux appear due to synergetic contribution between elastic and superelastic collisions. Eedf tends to increase its temperature and, when it is hot enough, the inelastic collisions prevail, determining a change in the eedf slope at the threshold of the first inelastic process. This behaviour is reflected on the level distribution (see fig 4 a), which cools till  $t=5 \cdot 10^{-8}$  s, because the energy is transferred to electrons through superelastic collisions, and later it is populated by inelastic collisions.

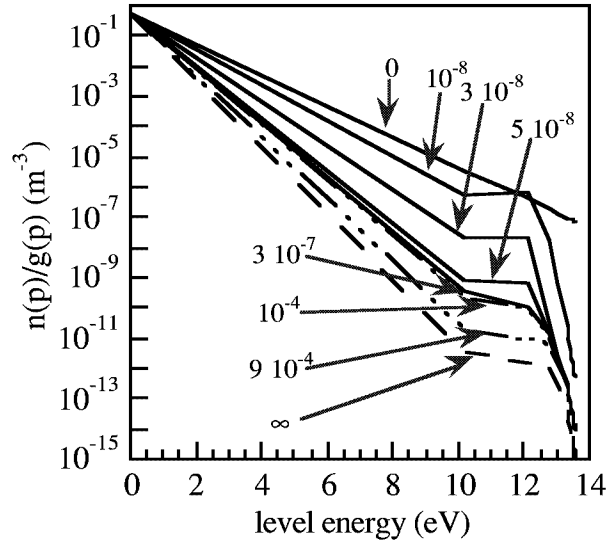


**FIGURE 3.** Time evolution of level distribution (a) and eedf (b) in the case 2 of table 1.



**FIGURE 4.** Time evolution of level distribution (a) and eedf (b) in the case 3 of table 1.

To study the role of non equilibrium electron distributions on level kinetics, we have performed calculations in the same condition of case 3 but fixing eedf to a maxwellian distribution at the initial electron temperature during all the temporal evolution. In this approximation, we neglect both eedf deviations from equilibrium and variations in electron temperature and consider constant rate coefficient for electron-atom collisions (see fig 5). Comparing fig 4 a with fig. 5, it can be noted that level population of fig 5 undergoes only a cooling and level population remain constant for  $10^{-7} \text{ s} \leq t \leq 10^{-8} \text{ s}$ , while in fig 4 a, in the same time interval, level population increases by 3-4 orders of magnitude. These results show that time dependent selfconsistent calculations are necessary to have an accurate study of the time evolution of level population.



**FIGURE 5.** Time evolution of level population in case 3 fixing eedf to a maxwellian distribution at the initial electron temperature

## CONCLUSIONS

Collisional-radiative model coupled, selfconsistently, with the solution of Boltzmann equation has been developed for hydrogen atoms. This model can be easily extended to other atomic systems and mixtures. Results have shown that, in particular when electron temperatures are low and electron density high, eedf differs greatly from equilibrium. Especially in these cases, time dependent selfconsistent calculations are necessary. In our numerical simulations, we have tried to understand the influence of the variation of some variables (e.g. gas and electron temperatures) over level populations and eedf. The conditions studied are a rough approximation of the behaviour of a plasma produced by laser ablation or LIBS. This last technique pretends to give quantitative analysis of surface composition and plasma temperature, making the assumption that the plasma is in local thermodynamic equilibrium (LTE) because the pressure is very high (1 atm). In this work we have shown that both in the heating and cooling phase the system is far to be in equilibrium. An improvement of the model could be found in a self-coupling with a fluid dynamic system, which should give more informations on the behaviours of the plasma produced by the interaction with a laser during the expansion (see for example [15,16]).

## ACKNOWLEDGMENTS

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